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Quantitative approaches to the determination of elements in lake sediments by total reflection X-ray fluorescence

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ABSTRACT

Element distribution data in lake sediments are widely used to study environmental and climate change over geological time scales. Total reflection X-ray fluorescence (TXRF) seems to be well suited for fast multi-elemental analysis of small quantities of subsamples obtained by cutting a sediment core at different intervals. The TXRF technique based on the direct analysis of a suspension prepared by mixing 20 mg of powdered sample and 2 mL of an aqueous 1% Triton X-100 solution was applied to the various reference materials of sedimentary rocks and samples of lake sediments to determine Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Ba contents. It was shown that the element internal standard, as well the Compton scattered peak, can be used to compensate the error associated with the sample deposition process. Different quantitative approaches have been proposed and evaluated using the reference materials of the sedimentary rocks: (i) internal standardization, (ii) external calibration with correction by means of adding an internal standard, (iii) external calibration with the 'fluorescent-to-Compton' correction. It was shown that the external calibrations can compensate systematic overestimation or underestimation of the TXRF results obtained using the internal standard method, especially for Al, K, V, Cr, Zn, Rb, and Ba. The TXRF results for Ca, Ti, Mn, Fe, Ni, Cu, and Sr weakly depend on the quantitative procedure.

1. Introduction

One of the most popular geological applications of X-ray fluorescence (XRF) spectrometry is the analysis of lake and ocean core sediments to study environmental and climate change over geological time scales [1]. Absolute changes in the element concentration with the depth of the core are obtained by means of analyzing dry, powdered, homogenized sediment fragments [2,3]. It is important to emphasize that complex high-resolution studies require analyzing large number of discrete samples, whose quantities are often limited (< 500 mg) [3,4]. From this point of view, total reflection X-ray fluorescence (TXRF) seems to be well suited for multi-elemental analysis of small quantities of subsamples obtained by cutting the sediment core at different intervals.

Reliable reconstructions of the environmental changes using element profiles are only possible if the errors owing to the sample preparation and quantification procedures are minimized. As it was shown in previous studies [5–15], the preparation of solid samples as slurries before TXRF is a good alternative to digestion procedures. Commonly, 10–50 mg of a powdered sample is applied to preparing suspension. Analytical approaches based on the direct analysis of a solid suspension by TXRF and the quantification by the internal standard method is carefully described in the literature for various types of complex samples. However, the reliable quantification of some elements is still problematic due to the absorption effects, especially in low-Z region of the TXRF spectra [11,12,14], as well as the instability of solid suspensions [14]. Moreover, particle size, mineralogy and morphology effects as well as inaccurate deconvolution of the TXRF spectra due to the overlaps between analyte and pile-up peaks, can lead to either under- or overestimation of the true concentration of the analyte [5,8,13,15]. To overcome the difficulties associated with the quantitative analysis of slurries, some procedures applied, for example, external calibration for K and Ca in food [11], applying a correction factor in the analysis of human placenta samples [12] and building materials [14], recalibration of spectrometer using real samples with known element concentrations [5].

TXRF advantages such as the possibility of fast elemental analysis of small sample amounts prepared as slurries let us to apply this technique to the determination of Br in the sediment core [4]. The goal of the present research is to minimize the error in the quantification of the expanded set of the elements of interest (Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Ba). Different quantitative approaches have been proposed and evaluated using the reference materials of the sediments: (I) internal standardization, (II) external calibration with the correction by means of adding an internal standard to the sample, (III) external calibration with the ratio of the fluorescent peak to the Compton scattered peak. The fluorescence-to-Compton ratio has been widely used in the analysis of organic and mineral samples by conventional XRF to compensate matrix effects and variations of the sample mass and density. In the TXRF analysis, the fluorescence-to-Compton ratio was successfully applied to organic samples, e.g. diesel fuel [16], petroleum crude oil [17], blood serum and human brain [18,19], instead of the quantification based on the adding internal standard. To our knowledge, there are no published scientific contributions about the using Compton peak in the quantitative analysis of the sediments by TXRF.

2. Materials and methods

2.1. Instrumentation

The measurements were performed using a benchtop S2 PICOFOX™ TXRF-spectrometer (Bruker Nano GmbH, Germany) equipped with a micro-focus X-ray tube with a Mo-anode and air cooling, a planar multilayer monochromator (Ni/C), and a Si drift detector (SDD) XFlash® with an area of 30 mm^2 and 150 eV resolution for the MnKα-line. All measurements were conducted at 50 kV operating voltage and 750 μA current. The measurement time was 1000 s per sample. The treatment of the X-ray spectra and the calculations were performed using the software SPECTRA 6 with the deconvolution based on a Bayesian inference (Super Bayes). The intensity of the Compton scattered peak was selected around the region of interest (ROI) at 16.9 keV.

2.2. Geological reference materials

We used the certified reference materials of Baikal bottom silts (BIL-1, BIL-2), carbonate, terrigenous and anomalous silts (SGH-1, SGH-3, SGH-5), carbonate, carbonate silicate and aluminosilicate loose sediments (SGHM-1, SGHM-2, SGHM-3, SGHM-4), which were produced and certified by Vinogradov Institute of Geochemistry of Siberian Branch of the Russian Academy of Sciences [20]. The certified reference materials of clays, slits and ooze (SDO-1 (OOPE101), SDO-3 (OOPE401), SDO-8 (OOPE402), SDO-9 (OOPE501)) were produced and certified by the Research Institute of Applied Physics (RIAP) at Irkutsk State University (Russia) [20]. Also for the study, the reference materials such as CH-1 (marine sediment, GeoPT-10), MSAN (ocean floor sediment, GeoPT-15) and SdAR-1 (modified river sediment, GeoPT-31) were provided by the International Association of Geoanalysts [20].

2.3. Samples

Samples in an amount of 50 pieces were divided from the sediment core of Lake Khara-Nur (Eastern Sayan Mountains, Russia) [4,21], dried at 50–60 °C and homogenized using an agate mortar with a pestle. Because only small amount of the sample are analyzed by TXRF, the sample must be homogenous to ensure representative results [5]. Particle size in the studied sediment powders was examined using the diffraction analysis by a Laser Particle Sizer "ANALYSETTE 22" Compact (Fritsch GmbH). According to the measurements, the average particle size is 15–20 μm, which is acceptable for the TXRF technique [10,15].

Table 1
Relative standard deviations (%) of ten replicates prepared from the reference materials SGH-3 (background silt) and SDO-1 (terrigenous clay).

Element	SGH-3			SDO-1		
	I_i	I_i/I_{Ga}	I_i/I_{inc}	I_i	I_i/I_{Ga}	I_i/I_{inc}
Al	16	4.3	4.8	17	3.7	3.6
K	15	3.0	2.7	16	2.4	2.1
Ca	13	5.4	6.1	15	6.5	6.3
Ti	17	6.6	5.5	16	3.1	3.4
V	15	6.1	4.7	16	4.4	4.7
Cr	14	5.3	5.1	16	2.7	2.8
Mn	13	2.9	2.2	16	6.0	6.5
Fe	13	3.4	2.7	15	1.9	2.5
Ni	16	4.8	3.6	16	2.6	2.6
Cu	15	3.8	3.3	15	3.1	3.5
Zn	14	4.2	3.6	16	2.3	2.8
Rb	15	4.8	3.0	19	3.4	2.8
Sr	13	5.8	4.4	15	2.6	2.7
Ba	15	4.7	4.6	17	1.8	2.2

2.4. Sample preparation

The solid suspensions were prepared by weighting 20 mg of the powdered samples and adding 2 mL of a 1% non-ionic surfactant Triton X-100 solution (reagent grade, Amresco) as a dispersing agent [4]. The Ga standard solution with concentration of 100 mg/L was prepared from the Ga stock solution with concentration of 1000 mg/L (CertiPUR®, Merck). A volume of 200 μL of the Ga solution of 100 mg/L was added to the 2 mL of the suspension as the internal standard, so that the final Ga concentration in the dried sample residue would be 1000 ppm. The resulting mixture was thoroughly homogenized and 10 μL of the suspension was pipetted onto a quartz glass carrier and dried at room temperature.

2.5. Quantification by TXRF

The quantitative analysis by TXRF is usually accomplished by the internal standardization based on the adding some element that is not initially present in the sample. In our study, a known amount (C_{Ga}) of the Ga solution was added into each sample since Ga was not detected in the original samples and the Ga concentration in the reference materials is < 10 mg/kg. The concentration of unknown element C_i is calculated using the relation:

$$C_i = \frac{I_i/S_i}{I_{Ga}/S_{Ga}} C_{Ga},$$ (1)

where I is the net intensity; S is the instrumental sensitivity. The manufacturer software SPECTRA 6 contains database of the sensitivity factors (S) calibrated at factory for Kα- and Lα-lines of elements from Al to U. According to the manufacturer's recommendations, the S2 PICOFOX spectrometer does not require any recalibration of the sensitivities.

Two variants of external calibrations using reference materials of the sediments were considered. The first calibration procedure involved the construction of the calibration curves by plotting the ratio of I_i/I_{Ga} against the reference concentrations:

$$C_i = a \cdot I_i/I_{Ga} + b,$$ (2)

where a is a slope, b is an intercept for the linear regression.

The second calibration procedure was based on the relationship between the ratio of the analyte to the Compton peak intensities (I_i/I_{inc}) and the reference concentrations:
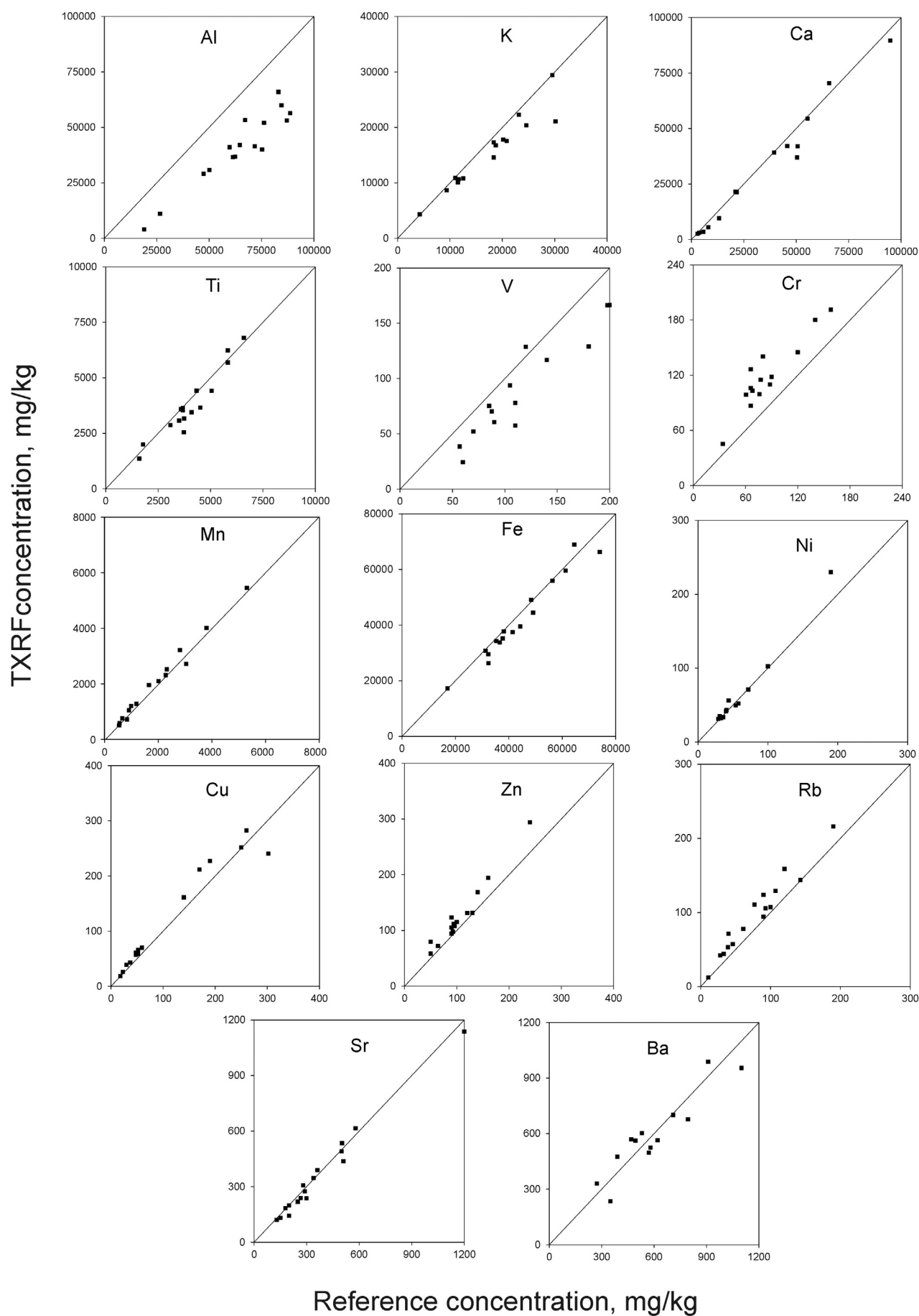
$$C_i = a \cdot I_i/I_{inc} + b$$ (3)

Fig. 1. Correlation between the concentrations determined by the internal standardization and the reference values.

Table 2
Parameters for linear regression analysis ($C_{Ref} = a \cdot C_{TXRF}$) and differences between the certified values and the data obtained by the internal standardization for the reference materials.

Element	Range, mg/kg	Slope a	R^2	RPD, %		
				Min	Max	Mean
Al	19,053–88,702	0.652	0.831	−58	−21	−37
K	4234–30,159	0.871	0.908	−30	2.5	−10
Ca	2522–285,262	0.995	0.995	−7	32	11
Ti	1605–6592	0.949	0.905	−19	12	−5
V	57–200	0.709	0.871	−59	7	−24
Cr	34–158	1.353	0.766	20	75	40
Mn	550–13,709	1.173	0.986	−12	33	8
Fe	17,066–82,673	0.938	0.953	−19	7	−6
Ni	29–370	1.170	0.993	−10	24	4
Cu	18–320	1.083	0.937	−20	30	14
Zn	50–240	1.176	0.962	5	37	16
Rb	11–190	1.180	0.932	1	43	22
Sr	130–1200	0.965	0.981	−28	10	−5
Ba	273–1500	0.975	0.928	−33	22	0.5

3. Results and discussion

3.1. Depositional repeatability

The depositional repeatability is the main contribution to the uncertainty budget [22]. In the case of the analysis of suspensions, the mass variations of the deposited solid depend on the stability of the prepared suspension as the concentration of solid particles can vary in different part of the vial due to the sedimentation process. It is assumed that the internal standardization corrects errors due to the sample preparation if the internal standard is homogenously distributed within the dried specimen. It can be demonstrated by the following assumptions. The sample on the carrier may be represented in the form of a thin cylinder. For excitation geometry of the TXRF-instrument, the equation for the dependence of the fluorescence intensity (I_i) on the size of the solid specimen deposited on the carrier is expressed with the accuracy up to a constant factor in the following form [23]:

$$I_i \approx const \cdot C_i \frac{1 - \exp(-\mu_{m1} \rho D)}{\mu_{m1} \rho D} \cdot \frac{1 - \exp(-\mu_{mi} \rho d)}{\mu_{mi}}, \qquad (4)$$

where C_i is the analyte concentration; μ_{m1} and μ_{mi} are the mass attenuation coefficients of the primary monochromatic MoKα radiation and fluorescence radiation of the analyte i; ρ is the density of the sample; d is the thickness of the thin layer; and D is the diameter of the cylindrical sample.

If 10 µL of the suspension prepared from 20 mg of a sample is pipetted on the carrier, the surface density of the dried sample with a diameter of 5–6 mm is $\rho d \sim 3.5$–5.0 µg/cm^2. As exemplified by the SGH-3 reference material, it was calculated that the value $\mu_{mi} \rho d$ is < 0.2 for the analytical lines of the elements with atomic number $Z \geq 20$ (Ca) and, therefore, $1 - \exp(-\mu_{mi} \rho d) \approx \mu_{mi} \rho d$. For the primary radiation of the MoKα line, it was obtained that $\mu_{m1} \rho D > 7$ and $1 - \exp(-\mu_{m1} \rho D) \approx 1$. Under such conditions, Eq. (4) shows that the fluorescence intensity of both the analyte (i) and the internal standard of Ga are proportional to the surface density of the sample and, accordingly, they are proportional to the mass of the deposited sample. In this approximation, the ratio of I_i/I_{Ga} depends mainly on the content of the analyte and takes into account the deposited mass variations, even though thin film approximation may not be observed.

A number of the case studies [18,19] demonstrated that the incoherent or Compton peak of the TXRF spectrum can be successfully used as an internal standard for biological materials because the Compton scattered signal is also proportional to the specimen mass. Under the conditions described above, the Compton scattering intensity (I_{inc}) is presented in the form of Eq. (4) if the C_i value will be replaced by the differential incoherent scattering coefficient do_{inc}^m, which weakly depends on the sample composition. Thus, the value of I_{inc} is also proportional to the surface density of the sample and the ratio of I_i/I_{inc} depends only on the content of the analyte.

In order to test the repeatability of the sample deposition process, 10 replicates were prepared from the reference materials SGH-3 (background silt) and SDO-1 (terrigenous clay) and measured once. Table 1 presents the relative standard deviations (RSD) between the measurements of 10 independent replicates. The RSD values were calculated using the measurement results of the net fluorescent intensity of an analyte (I_i), the ratio of I_i/I_{Ga}, and the ratio of I_i/I_{inc}. It is clear from Table 1 that the repeatability of the sample deposition is worse (13–19%) when the net peak of the analyte was measured. This is due to the fact that it is quite difficult to achieve an exact reproduction of the positioning and uniform distribution of the solid sample placed on the carrier [15]. A significant reduction of the RSD values is achieved when using normalization to the internal standard of Ga or to the Compton peak. Using both ratios I_i/I_{Ga} and I_i/I_{inc} gives similar acceptable uncertainties, which are generally better than 7% for all elements of the interest. The intensities ratio compensates the deviations in the measurements and the variations in the sample mass dried on the carrier. It is demonstrated that the Ga internal standard as well the Compton peak can be used to compensate the error associated to the sample deposition process.

To estimate the instrumental precision, one of the replicates of the SGH-3 and SDO-1 was measured ten times. It was found that the RSD values was < 1% for most elements, except V (4%), Cr (2%) and Ba (5%). It indicates good instrumental stability and reliable counting statistics.

As a rule, the reference materials of the sediments are well-ground and homogenized powders. To assess the heterogeneity of the real samples of the sediments, 20 independent suspensions were prepared from the sample powder of 400 mg. An aliquot of each suspension was measured once. The RSDs between 20 measurements were calculated using I_i/I_{Ga} or I_i/I_{inc} ratios and their values varied in the range of 5–12% depending on the element determined. These values include the error associated with the sample heterogeneity as well as with the sample deposition error. Since a very small amount of the investigated material on the carrier was measured by TXRF, we assumed that this level of uncertainty is satisfactory.

### 3.2. Comparing the quantitative approaches

The reference materials of the sediments in an amount of 16 pieces were prepared as a duplicate and measured by TXRF. The internal standard method described in the Section 2.5 was applied to all reference materials as the quantitative strategy widely used in TXRF. In Fig. 1 a series of diagrams have been plotted with the TXRF results (C_{TXRF}) obtained by the internal standardization versus the certified values (C_{Ref}). The TXRF concentration represents the average concentration from duplicate samples. It was assumed that if the certified concentration approaches zero, the concentration obtained by TXRF also approaches zero. Parameters of a linear regression with the intercept equal to zero ($C_{Ref} = a \cdot C_{TXRF}$) are presented for each element of interest in Table 2.

A relative percentage difference (RPD) between the concentration determined by internal standardization (Eq. (1)) and the reference values were calculated using the following formula:

$$RPD = \frac{C_{TXRF} - C_{Ref}}{C_{Ref}} \cdot 100\% \qquad (5)$$

We suppose that the TXRF data is accurate if the measured value is not more 20% of the certified value for the reference material.

As it can be seen from Fig. 1 and Table 2, a good correlation between the TXRF data and the certified values ($R^2 > 0.90$, $a = 0.9$–1.1)

Concentration, mg/kg
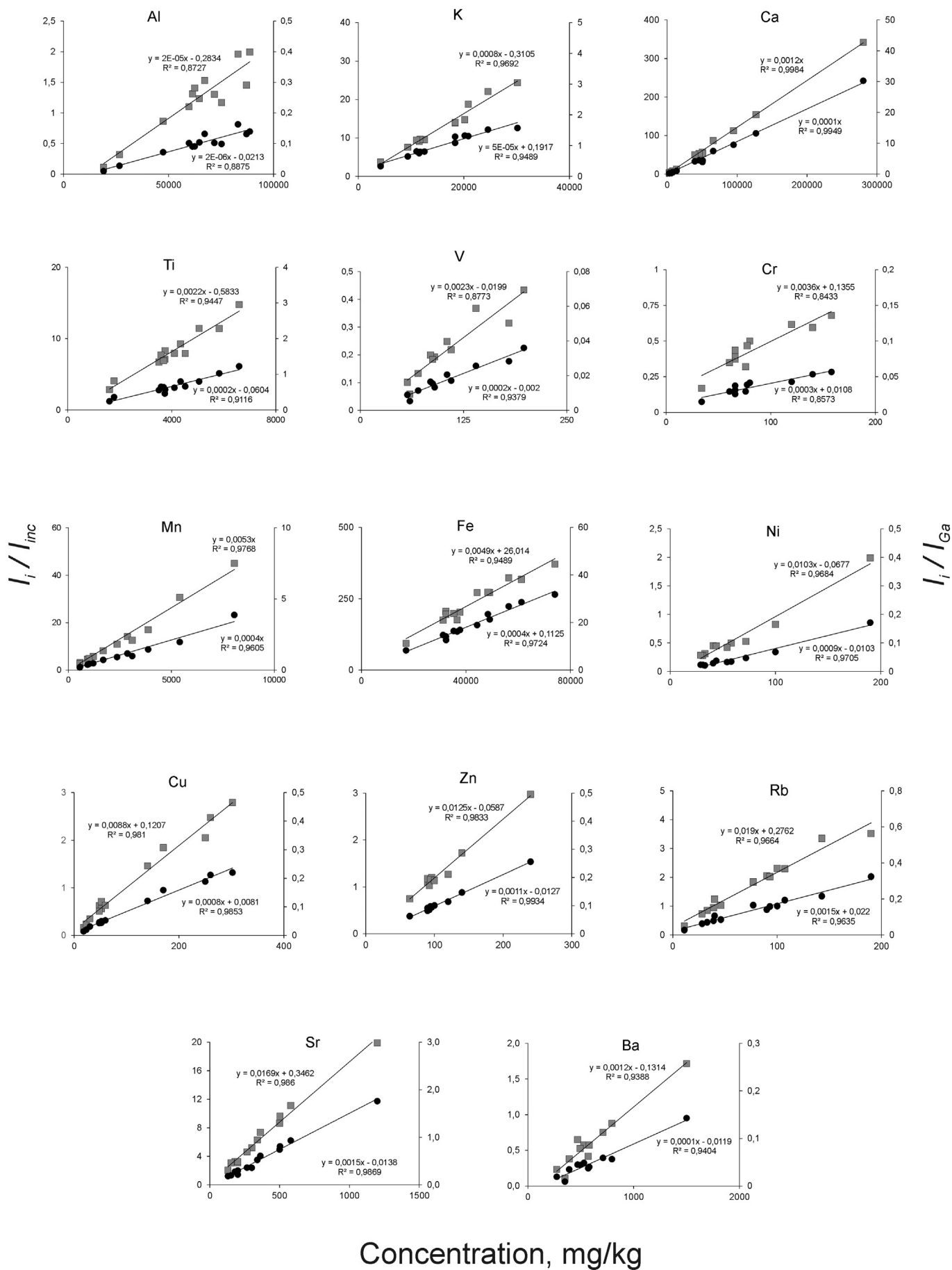
(caption on next page)

Fig. 2. Calibration curves constructed using the reference materials by plotting the ratios of I_i/I_{Ga} (black circle) or I_i/I_{inc} (grey square) against the reference concentrations.
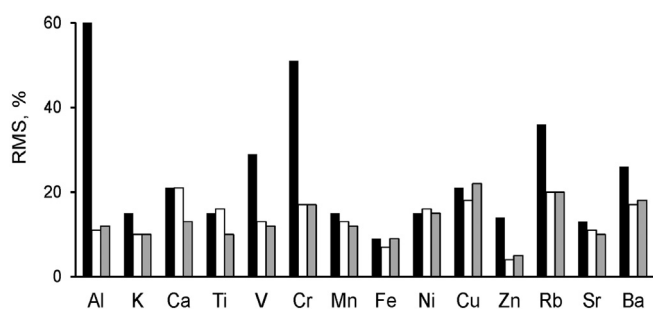
Fig. 3. The *RMS* values obtained by the internal standard method (black boxes), external calibrations $I_i/I_{Ga} = f(C_{Ref})$ (white boxes) and $I_i/I_{inc} = f(C_{Ref})$ (grey boxes).

is observed for Ca, Ti, Fe, Cu, Sr, and Ba. For Mn, Ni, Zn, and Rb the correlation coefficient value is high ($R^2 > 0.93$), but the slope is > 1.1, reflecting slight overestimation of the obtained concentrations. The lowest correlation coefficient values ($R^2 < 0.90$) and the highest mean values of the *RPD* were found for Al, V and Cr. The slope value for Al are significantly lower than 1.0 ($a = 0.652$) and is explained by the measurements in air and the absorption effects in low-Z region of the TXRF-spectra. For the same reason, some underestimation of K ($a = 0.871$) is explained also. Poor linearity and the underestimation of V ($a = 0.709$) and overestimation of Cr ($a = 1.353$) probably related to the mineralogical effects as these elements are often presented in accessory minerals.

We assumed that the external calibration could compensate systematic overestimation or underestimation of the TXRF results obtained using the internal standard method because of acceptable linear relationship between the certified and the TXRF data was established for most elements of interest. Two variants of external calibrations were proposed. Calibration curves $I_i/I_{Ga} = f(C_{Ref})$ and $I_i/I_{inc} = f(C_{Ref})$ presented in Fig. 2 were established using all reference materials except SGH-1, SDO-9 and SGH-5, which were chosen to control the accuracy of the external calibrations. The form of the linear regression equation (Eq. (2) and Eq. (3)) was chosen to provide the minimum value of the standard deviation characterizing a dispersion of points around the calibration line over the concentration range. For Al, K, Ti, V, Cr, Zn and Rb a linear regression line had an equation with intercept different than zero, for other elements a linear regression was chosen with the intercept equal to zero.

As it can be seen from Fig. 2, a good linearity ($R^2 \geq 0.94$) was obtained for most elements regardless of the used normalization. The lower correlation coefficients ($R^2 \sim 0.84$–0.89) were observed for Al, V, and Cr.

Using the linear regression parameters (slope, intercept) of the calibration functions presented in Fig. 2, the element concentrations were calculated for all calibration samples. To compare the quantitative approaches, the root mean square (*RMS*) was estimated according to the following equation:

$$RMS = \sqrt{\frac{1}{N} \sum \left(\frac{\widehat{C}_{TXRF} - C_{Ref}}{C_{Ref}} \right)^2} \cdot 100\% \tag{6}$$

where $\widehat{C}_{TXRF}$ is the calculated concentration of the element, N is the number of samples ($N = 13$).

Fig. 3 presents the *RMS* values characterizing differences between the recommended concentrations in calibration samples, and the TXRF values obtained by the internal standard method (I), external calibration $I_i/I_{Ga} = f(C_{Ref})$ (II) and external calibration $I_i/I_{inc} = f(C_{Ref})$ (III). In view of the data presented in Fig. 3, we consider that the external calibrations (II) and (III) may be useful to improve the results of the determinations of Al, K, V, Cr, Zn, Rb, and Ba contents. This fact confirms lower *RMS* values achieved using the external calibrations for the quantification in comparison with the values obtained for the analysis by the internal standardization. The *RMS* values for Ca, Ti, Mn, Fe, Ni, Cu, and Sr are weakly depended on the quantitative procedure.

The accuracy of the proposed external calibrations $I_i/I_{Ga} = f(C_{Ref})$ and $I_i/I_{inc} = f(C_{Ref})$ was verified by the certified reference materials SGH-1, SDO-9 and SGH-5 that were not included in derivation of the linear-regression curves (Table 3). As we have duplicate measurements (C_1 and C_2) of 16 reference materials, including 13 calibration samples and 3 samples for the accuracy control ($N = 16$), the confidence interval (ΔC_i) of the calculated TXRF concentration (C_i) was estimated as:

$$\Delta C_i = t(0.05, f) \cdot S_d / \sqrt{n} \tag{7a}$$

$$S_d = CV \cdot C_i \tag{7b}$$

$$CV = \sqrt{\frac{1}{N} \sum \left(\frac{2}{\sqrt{2}} \frac{|C_1 - C_2|}{(C_1 + C_2)} \right)^2} \tag{7c}$$

where S_d is the standard deviation, $f = N(n-1)$ is the degrees of freedom associated with S_d, n is number of replicate measurements of the sample ($n = 2$), CV is the coefficient of variation evaluated from several pair of

Table 3
The accuracy control of the proposed external calibrations $I_i/I_{Ga} = f(C_{Ref})$ and $I_i/I_{inc} = f(C_{Ref})$ by the analysis of the certified reference materials SGH-1, SDO-9 and SGH-5.

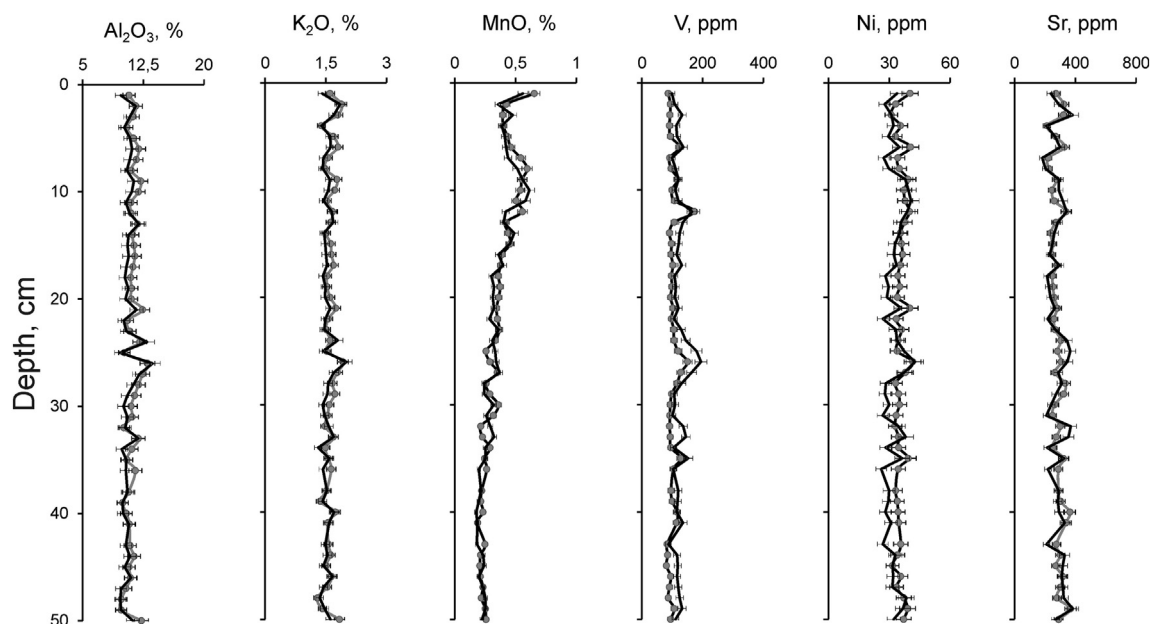| Analyte	SGH-1			SDO-9			SGH-5		
	Certified	I_i/I_{Ga}	I_i/I_{inc}	Certified	I_i/I_{Ga}	I_i/I_{inc}	Certified	I_i/I_{Ga}	I_i/I_{inc}
Al_2O_3 (%)	9.48 ± 0.14	9.98 ± 0.75	10.10 ± 0.76	15.97 ± 0.14	16.35 ± 1.23	14.51 ± 1.09	14.40 ± 0.11	14.65 ± 1.10	13.26 ± 0.99
K_2O (%)	2.26 ± 0.07	2.44 ± 0.11	2.32 ± 0.10	2.79 ± 0.06	3.2 ± 0.14	2.51 ± 0.11	3.56 ± 0.09	3.77 ± 0.17	3.46 ± 0.16
CaO (%)	7.76 ± 0.10	7.63 ± 0.69	7.71 ± 0.76	3.03 ± 0.10	2.98 ± 0.27	2.68 ± 0.24	2.95 ± 0.05	3.03 ± 0.27	2.88 ± 0.26
TiO_2 (%)	0.50 ± 0.02	0.55 ± 0.06	0.56 ± 0.06	0.98 ± 0.01	1.06 ± 0.12	0.92 ± 0.10	0.62 ± 0.01	0.67 ± 0.08	0.60 ± 0.07
MnO (%)	0.30 ± 0.01	0.25 ± 0.03	0.26 ± 0.03	1.77 ± 0.03	1.76 ± 0.21	1.51 ± 0.18	0.087 ± 0.003	0.085 ± 0.01	0.075 ± 0.01
Fe_2O_3 (%)	5.92 ± 0.04	5.71 ± 0.51	5.86 ± 0.53	9.23 ± 0.07	10.1 ± 0.91	9.02 ± 0.81	5.45 ± 0.10	5.75 ± 0.52	5.03 ± 0.45
V (mg/kg)	110 ± 10	80 ± 10	83 ± 10	150 ± 20	168 ± 20	149 ± 18	110 ± 10	103 ± 12	94 ± 11
Cr (mg/kg)	68 ± 6	73 ± 10	76 ± 10	90 ± 10	110 ± 15	95 ± 13	88 ± 6	78 ± 11	70 ± 9
Ni (mg/kg)	40 ± 4	43 ± 5	42 ± 5	370 ± 30	339 ± 41	305 ± 37	36 ± 3	37 ± 4	31 ± 4
Cu (mg/kg)	37 ± 4	33 ± 3	34 ± 3	320 ± 30	370 ± 33	340 ± 30	190 ± 10	214 ± 19	195 ± 18
Zn (mg/kg)	50 ± 10	57 ± 5	57 ± 5	160 ± 20	165 ± 15	146 ± 13	90 ± 10	108 ± 10	98 ± 9
Rb (mg/kg)	61 ± 3	67 ± 5	68 ± 5	90 ± 7	103 ± 8	90 ± 7	120 ± 10	137 ± 10	119 ± 9
Sr (mg/kg)	250 ± 40	229 ± 24	238 ± 25	290 ± 30	297 ± 31	256 ± 27	280 ± 30	316 ± 33	288 ± 30
Ba (mg/kg)	620 ± 30	565 ± 85	563 ± 84	1100 ± 100	955 ± 140	850 ± 120	910 ± 70	988 ± 150	878 ± 132

Fig. 4. The distribution of elements in Lake Khara-Nur bottom sediments core (50 cm) determined by the external calibrations using I_i/I_{Ga} (grey) and I_i/I_{in} (black). Error bars represent the standard deviation of measuring duplicates.

duplicate results (C_1, C_2) [24,25].

Table 3 data show that the TXRF data obtained by the proposed external calibration methods are very close to the certified concentrations of the elements in the reference materials. The *RPD* values are within ± 20% for most elements. The concentration of V for SGH-1 are lower than the certified value (*RPD* = −25–27%) but when V was quantified by the internal standard method, the *RPD* value was −48%. Also some underestimation of Ba (*RPD* = −26%) in SDO-9 was observed when using external calibration $I_i/I_{inc} = f(C_{Ref})$.

Taking into account presented results, it was decided to apply both external calibration methods to the sediment samples instead of the internal standard method commonly used for the quantification in the TXRF spectrometry.

3.3. TXRF quantification of elements in sediment samples

A row of 50 sediment samples selected from the core of Lake Khara-Nur was analyzed by TXRF. The element concentrations were quantified using external calibrations ($I_i/I_{Ga} = f(C_{Ref})$ and $I_i/I_{inc} = f(C_{Ref})$) described in the previous section. Concentrations of the elements analyzed were in the ranges of 9.8–13% for Al_2O_3, 1.3–1.9% for K_2O, 2.3–3.4% for CaO, 0.9–1.2% for TiO_2, 57–108 ppm for Cr, 0.18–0.61% for MnO, 6.1–12.7% for Fe_2O_3, 87–194 ppm for V, 26–43 ppm for Ni, 12–38 ppm for Cu, 91–174 ppm for Zn, 63–157 for Rb, 182–400 ppm for Sr, 480–860 ppm for Ba.

As an example, Fig. 4 shows the changes in the concentrations of Al_2O_3, K_2O, MnO, V, Ni, and Sr with the depth of the 50 cm sediment core evaluated applying the external calibrations using I_i/I_{Ga} and I_i/I_{inc} ratios. As shown in Fig. 4, both quantitative procedures give similar distributions of the elements.

We estimated the difference between the TXRF results by calculating the coefficient of variation (%) according Eq. (7c), where C_1 and C_2 are concentrations obtained using $I_i/I_{Ga} = f(C_{Ref})$ and $I_i/I_{inc} = f(C_{Ref})$ respectively. The differences between concentrations obtained by different external calibrations were not > 12% (Al – 4.1, K – 4.9, Ca – 4.2, Ti – 4.5, V – 7.4, Cr – 9.5, Mn – 11, Fe – 9.4, Ni – 9.2, Cu – 10, Zn – 10, Rb – 12, Sr – 9.5, Ba – 10).

4. Conclusions

In the present study, we compared different quantitative approaches to the determination of the elements of interest in the lake sediments: the internal standardization, the external calibration with the correction by adding the Ga internal standard, the external calibration with the 'fluorescent-to-Compton' correction. It was demonstrated that the normalization of the net intensity analytical signal to the incoherent scattered signal (Compton peak) could reduce the uncertainties associated with the sample preparation process. Similar repeatability (generally better than 7%) was obtained using the normalization with the Ga internal standard or the Compton peak.

Two variants of the external calibrations with the ratio of the fluorescent peak to the internal standard peak or the Compton scattered peak were proposed to quantify Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Ba in sediments by TXRF. Comparative study of the quantitative procedures showed that the external calibrations is a good option to improve the TXRF results of Al, K, V, Cr, Zn, Rb, and Ba determinations. The results of Ca, Ti, Mn, Fe, Ni, Cu, and Sr determinations weakly depend on the quantitative procedure and can be estimated by the internal standard method as well as external calibrations. The proposed method of calibration using the Compton peak eliminates the need adding the internal standard to the sample. The limitation of the external calibration methods is the need to have calibration samples with matrix similar analyzed samples but it is important to note that a wide set of the reference materials of the sedimentary rocks with the certified data regarding Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Ba are available.

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